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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/IL98/00177 <b>(22) International Filing Date:</b> 14 April 1998 (14.04.98) <b>(30) Priority Data:</b> 120802                      8 May 1997 (08.05.97)                      IL <b>(71) Applicant (for all designated States except US):</b> BEN GURION UNIVERSITY OF THE NEGEV RESEARCH AND DEVELOPMENT AUTHORITY [IL/IL]; P.O. Box 653, 84105 Beer Sheva (IL). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> MARKUS, Arie [IL/IL]; Bialik Street 151/21, 84308 Beer Sheva (IL). <b>(74) Agent:</b> WOLFF, BREGMAN AND GOLLER; P.O. Box 1352, 91013 Jerusalem (IL).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> A PROCESS FOR ENCAPSULATING LAYGON		
<b>(57) Abstract</b>  The invention provides a process for encapsulating a mixture of propoxur, tetramethrin, piperonyl butoxide, N-octyl-bicycloheptene-dicarboximide (MGK) and essential oil of lemon (laygon) in a micro-capsular formulation comprising providing a first solution of water and polyvinyl alcohol (PVA) and heating to about 50–60 °C, providing a second organic solution comprising a mixture of melted laygon and an isocyanate, emulsifying the second mixture in the first mixture, adding an aqueous solution of a polyfunctional amine with agitation to the emulsion the solution containing about 10 % – 40 % of the stoichiometric amount by weight of amine necessary to fully react with the isocyanate, adding an oxyethylated monooleate sorbate emulsifier to prevent coagulation of the reaction mixture, adding the remaining polyfunctional amine solution over a period of between 5 to 10 minutes, reducing the temperature of the reaction mixture to about 20° – 40° CO, and adding a weak polyfunctional acid to neutralize the solution to a pH of about 7.0–8.0.		

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## A PROCESS FOR ENCAPSULATING LAYGON

The present invention relates to pesticidal composition and to a process for the preparation thereof.

More particularly, the present invention related to a pesticidal composition comprising a mixture of propoxur, tetramethrin, piperonyl butoxide, N-octyl-bicycloheptene-dicarboximide (MGK) and essential oil of lemon which mixture is known as and will be referred to hereinafter as laygon as active ingredient therein and to a process for encapsulating laygon in a micro-capsular formulation.

The encapsulating of various chemical reagents, pharmaceuticals, pesticides and herbicides in general have been proposed and described in the prior art.

As described e.g. in U. S. Patent 4,417,916, aqueous dispersions of pesticide and herbicide micro-capsules are particularly useful in controlled release pesticidal and herbicidal formulations because they can be diluted with water or liquid fertilizer and sprayed using conventional equipment, thereby producing uniform field coverage of the pesticide or herbicide/additives such as film forming agents can be added directly to the finished formulation to improve the adhesion of micro-capsules to foliage. In some cases, reduced toxicity and extended activity of encapsulated herbicides and pesticides have been noted.

A variety of techniques have heretofore been used or proposed for encapsulation purposes. In one such process, known as "simple co-acervation", a polymer separates from a solvent solution of the polymer by the action of a precipitating agent that reduces the solubility of the polymer in the solvent (e.g., a salt or a non-solvent for the polymer). Patents describing such processes and their shell wall material includes U. S. Patent Nos. 2,800,458 (hydrophilic colloids); 3,069,370 and 3,116,216 (polymers); 3,137,631 (denatured proteins); 3,418,250 (hydrophobic thermoplastic resins); and others.

Another method involves micro-encapsulation based on in situ interfacial condensation polymerization. British Patent No. 1,371,179 discloses a process which consists of dispersing an organic pesticide phase containing a polymethylene polyphenylisocyanate or toluylene diisocyanate monomer into an aqueous phase. The wall forming reaction is initiated by heating the batch to an elevated temperature at which point the isocyanate monomers are hydrolyzed at the

interface to form amines, which in turn react with unhydrolyzed isocyanate monomers to form the polyurea micro-capsulate wall. One difficulty with this method is the possibility of continued reaction of monomer after packaging. Unless all monomer is reacted during the preparation, there will be continued hydrolysis of the isocyanate monomer with evolution of CO<sub>2</sub>, resulting in the development of pressure when the formulation is packaged.

Various methods of encapsulation by interfacial condensation between direct-acting, complimentary reactions are known. Within these methods are reactions for producing various types of polymers as the capsule walls. Many of such reactions to reproduce the coating substance occur between an amine, which must be of at least di-functional character and a second reactant intermediate, which for producing a polyurea is a di-functional or polyfunctional isocyanate. The amines chiefly used or proposed in these methods are typified by ethylene diamine, having at least two primary amino groups. U. S. Patent No. 3,429,827 and U. S. Patent No. 3,577,515 are illustrative of encapsulation by interfacial condensation.

For example, U. S. Patent No. 3,577,515 describes a continuous or batch method which requires a first reactant and a second reactant complimentary to the first reactant, with each reactant in separate phases, such that the first and second reactants react at the interface between the droplets to form encapsulated droplets. The process is applicable to a large variety of polycondensation reactions, i.e., to many different pairs of reactants capable of interfacial condensation from respective carrier liquids to yield solid film at the liquid interface. The resulting capsule skin may be produced as a polyamide, polysulfonamide, polyester, polycarbonate, polyurethane, polyurea or mixtures of reactants in one or both phases so as to yield corresponding condensation copolymers. The reference describes the formation of a polyurea skin when diamines or polyamines (e.g. ethylene diamine, phenylene diamine, toluylene diamine, hexamethylene diamine and the like) are present in the water phase and di-isocyanates or polyisocyanates (e.g., toluene diisocyanate, hexamethylene diisocyanate and polymethylene polyphenylisocyanate) are present in the organic/oil phase. In the practice of U.S. Patent No. 3,577,515, the liquid which preponderate becomes the continuous phase liquid. That is, in forming oil containing micro-capsules, the aqueous liquid

would preponderate; when water encapsulated micro-capsule are formed, the oil phase would preponderate.

Of particular importance to note is that despite the general description in said patent, it specifically claims and is limited to the reaction of a polyisocyanate having at least three isocyanate groups or an isocyanate having less reactive groups in combination with another reaction intermediate such as an acyl halide, e.g., sebacoyl chloride, since a necessary condition for the reaction is the presence of at least three reactive groups.

On the other hand, U. S. Patent No. 4,417,916 claims a process of encapsulating water-immiscible material within a shell wall of polyurea which comprises:

- a. providing an aqueous phase containing an emulsified selected from the group consisting of sodium, potassium, magnesium, calcium or ammonium salts of lignin sulfonate;
- b. dispersing in said aqueous phase, a water-immiscible phase consisting essentially of polymethylene polyphenylisocyanate dissolved in said water-immiscible material, to form a dispersion of water-immiscible material, to form a dispersion of water-immiscible phase droplets throughout the aqueous phase; and
- c. adding, with agitation, to said dispersion a poly-functional amine, whereby said amine reacts with a polymethylene polyphenylisocyanate to form a polyurea shell wall about said water-immiscible material.

As will be noted, while said patent acknowledges and thus evidences clear awareness of the teachings of U. S. Patent No. 3,577,515, it is limited to the use of polymethylene polyphenylisocyanate which is a large polymer, not particularly stable and quite expensive.

In European Patent applications, Publication numbers 148,169 and 165,227 of Monsanto, as well as in Monsanto's U. S. Patent 4,563,212, there are described and claimed encapsulation systems utilizing an interfacial polycondensation reaction. All of said patents, however, are based on the use of only specific emulsifiers, i.e., alkylate polyvinylpyrrolidone polymers (EP 148,169 and 165,227) or sulfonated naphthalene formaldehyde condensates and sulfonated polystyrenes

(U. S. Patent 4,563,212) and this in light of the specific statement and teaching on page 8 of EP 0165227 that "experiments indicate that conventional oil/water herbicide emulsifiers fail to produce suitable emulsions for attaining micro-encapsulation of concentrated amounts of herbicidal material.

In Israel Patent 84219 there is provided a process for encapsulating alachlor or trifluralin in a micro-capsular formulation, comprising:

- a) providing an aqueous phase containing a non-basic emulsifier, said emulsifier being selected from the group consisting of low and high density polyvinylalcohol, tween 20, tween 40 or tween 80.
- b) providing an organic phase containing toluylenediisocyanate, hexamethylenediisocyanate or mixtures thereof and melted alachlor or melted trifluralin;
- c) combining said aqueous and organic phase to form an oil in water emulsion; and
- d) adding an aqueous solution of a polyfunctional amine with agitation to said emulsion, whereby said amine reacts with said toluylenediisocyanate, hexamethylenediisocyanate or mixtures thereof to form micro-capsular envelopes about said alachlor or trifluralin material.

However it has been found that none of the processes described in the prior art are effective for encapsulating laygon, since, as indicated, laygon is a mixture of components and it is difficult to effect encapsulation of all of the components of the mixture as opposed to one ingredient at a time. Furthermore, the encapsulation of carbamates is often not successful due to the reactive nature of the molecule. Moreover it was found, for example, that attempting to apply the procedure of Israel Patent 84218 to the encapsulation of laygon resulted in immediate aggregation without encapsulation of the active component. In addition, it was found that the presence of the emulsifier from the beginning of the reaction procedure also makes it impossible to form the capsules since a paste is formed instead.

With this state of the art in mind, there has now been found, according to the present invention, a process for encapsulating a mixture of propoxur, tetrametrin,



piperonyl butoxide, MGK and essential oil of lemon (laygon) in a micro-capsular formulation comprising:

- a) providing a first solution of water and polyvinyl alcohol (PVA) and heating to about 50-60° C;
- b) providing a second organic solution comprising a mixture of melted laygon and an isocyanate;
- c) emulsifying said second mixture in said first mixture;
- d) adding an aqueous solution of a polyfunctional amine with agitation to said emulsion said solution containing about 10% - 40% of the stoichiometric amount by weight of amine necessary to fully react with said isocyanate;
- e) adding an oxyethylated monooleate sorbate emulsifier to prevent coagulation of the reaction mixture;
- f) adding the remaining polyfunctional amine solution over a period of between 5 to 10 minutes;
- g) reducing the temperature of the reaction mixture to about 20° - 40° C; and,
- h) adding a weak polyfunctional acid to neutralize the solution to a pH of about 7.0-8.0.

In preferred embodiments of the present invention said aqueous solution in step d contains about 20% - 30% of the stoichiometric amount by weight of amine necessary to fully react with said isocyanate;

In further preferred embodiments of the present invention at least one UV absorbent material is included in the organic solution of step b.

In yet a further embodiment of the present invention there is included an additional step of adding a mixture of propylene glycol, soap and gums, said gums preferably being selected from the group consisting of xanthan, guar, caraya and mixtures thereof.

Said polyfunctional acid used in step h is preferably selected from the group consisting of citric acid, ascorbic acid and phosphoric acid.

While the invention will now be described in connection with certain preferred embodiments in the following examples so that aspects thereof may be more fully understood and appreciated, it is not intended to limit the invention to

these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims. Thus, the following examples which include preferred embodiments will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purposes of illustrative discussion of preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of formulation procedures, as well as of the principles and conceptual aspects of the invention.

### Examples

A plurality of various formulations containing Laygon as the active ingredient therein and using different isocyanates and different polyfunctional amines to encapsulate the same were prepared according to the following procedure:

A first solution designated A which consists of PVA and water is heated to 55 °C. A second solution designated B is prepared consists of a melted mixture of propoxur, tetramethrin, MGK, and piperonyl butoxide to which at first at least one U. V. absorber (Tinuvin<sup>®</sup> by Ciba-Geigy) is added until a clear solution is formed and then lemon oil and at least one isocyanates are added). Solution B is emulsified in solution A. A further solution C consisting of an aqueous solution of a polyfunctional amine is then added, said solution containing about 25% of the stoichiometric amount by weight of amine necessary to fully react with said isocyanate. After adding approximately 1/4 of the amine solution, tween 80 is added in order to prevent conglomeration of the reaction mixture. Then the rest of solution c is added. The temperature is dropped to 40 °C and mixed for two hours. Citric acid is added to bring the pH to 7.5 and solution D consisting of propylene glycol, soap and gums (xanthan or guar or caraya) is added. The reaction mixture is stirred for another 15 minutes and then put in bottles.

The formulations are summarized in Table 1:

Table 1 COMPOSITIONS OF LAYGON FORMULATIONS

Example no.	Isocyanate		Copolymer polyester		Amines or Alcohols		HPLC (%)
	Type	Amount g	Type	Amount g	Type	Amount g	
Pro-1	Vorunate M-580	42	-	-	TEPA + DETA +	9.6 + 6.2	17.4
Pro-2	Vorunate M-580	10	Bayflex 2200 B	30	1,4-BD + TMP	2 + 0.7	-
Pro-3	Vorunate M-580	17	Bayflex 2200 B	18	-	-	17.6
Pro-4	Vorunate M-580	42	-	-	EDA + DETA	3 + 2	19.8
Pro-5	Vorunate M-580	24	Bayflex 2200 B	12	- 1,4-BD	1	19.7
Pro-6	Vorunate M-580	12	Bayflex 2200 B	24	-	-	18.5
Pro-7	Vorunate M-580	27	Bayflex 2200 B	9	EDA + DETA	2.2 + 2.5	21.6
Pro-8	Vorunate M-580	27	Bayflex 0549	9	EDA + DETA	2.2 + 2.5	20.4
Pro-9	Vorunate M-580	20	Bayflex 0549	16	1,4-BD	1	18.5
Pro-10	Vorunate M-580	24	Bayflex 0549	12	TMP	1	9.3
Pro-11	Isonate M-301	20	Bayflex 0549	1.6	1,4-BD	1	-
Pro-12	Isonate M-301	24	Bayflex 0549	12	TMP	1	14.5
Pro-13	Vorunate M-580	35	-	-	HMDA	7	18.7
Pro-14	Vorunate M-580	35	-	-	1,4-Ph DA	6.5	18.1
Pro-15	Vorunate M-580	34	Bayflex 2200 B	6	1,4-BD + TMP	1 + 1	16.3
Pro-16	HMDI	6	Bayflex 0631	30	HMDA	1	-
Pro-17	Vorunate M-580	42	-	-	HMDA + DETA	6 + 5.5	20.5
Pro-18	Isonate M-342	42	-	-	DETA + PDA	5.5 + 5	10.9
Pro-19	Isonate M-342	42	-	-	HMDA	5.5	18.2
Pro-20	Isonate M-301	42	-	-	-	-	14.1
Pro-21	Vorunate M-580	45.5	-	-	HMDA	6.5	-
Pro-22	Isonate M-304	42	-	-	HMDA	6.5	20.3
Pro-23	Vorunate M-580	42	-	-	-	-	14.9
Pro-24	Vorunate M-580	35	-	-	HMDA + TEPA	8 + 4	19.4
Pro-25	Vorunate M-580	42	-	-	HMDA + DETA	6 + 5.5	18.3
Pro-26	Isonate M-342	42	-	-	DETA + TEPA	5.5 + 9.3	19.3
Pro-27	Vorunate M-580	210	-	-	HMDA + DETA	30 + 17.5	20.4
Pro-28	Vorunate M-580	42	-	-	DETA + TEPA	6.3 + 9.6	19.2
Pro-29	Vorunate M-580	42	-	-	DETA + EDA	6.3 + 7.4	19.0
Pro-30	Vorunate M-580	42	-	-	1,4-BD + TMP	9.3 + 7.4	-
Pro-31	Vorunate M-580	210	-	-	HMDA + DETA	30 + 17.5	-
Pro-32	Isonate M-301	42	1,4-BD + TMP	3.3 + 7.4	-	-	-
Pro-33	Vorunate M-580	42	TMP	4	EDA + DETA	4 + 3	19.3
Pro-34	Isonate M-342	42	-	-	EDA + DETA	7.4 + 6.3	-
Pro-35	Vorunate M-580	42	-	-	EDA + TEPA	5.7 + 9.6	-
Pro-36	Isonate M-342	42	-	-	EDA + DETA	7.4 + 6.3	-
Pro-37	Isonate M-342	42	-	-	EDA + TEPA	5.7 + 7.0	-
Pro-38	Isonate M-342	42	-	-	EDA + DETA	3 + 6.3	-
Pro-39	Vorunate M-580	20	PEG-300	20	-	-	-
Pro-40	Vorunate M-580	20	PEG-500	20	EDA	19.5	-
Pro-41	Vorunate M-580	20	PEG-200	20	EDA	2	18.3

Table 1 COMPOSITIONS OF LAYGON FORMULATIONS (continued)

Example no	Isocyanate		Copolymer polyester		Amines or Alcohols		HPLC (%)
	Type	Amount	Type	Amount	Type	Amount	
Pro-42	Voranate M-580	15	PEG-600	20	TMP + EDA	1 + 1	16.9
Pro-43	Voranate M-580	20	PEG-400	15	-	-	17.9
Pro-44	Isonate M-342	42	-	-	HMDA + DETA	6.5 + 3.5	13.7
Pro-45	Isonate M-342	20	PEG-400	15	DETA	3.7	-
Pro-46	Isonate M-301	42	-	-	HMDA + DETA	4.5 + 3.5	-
Pro-47	Isonate M-310	42	-	-	HMDA + DETA	6.5 + 3.5	-
Pro-48	Isonate M-301	35	-	-	HMDA + DETA	4.5 + 2	18.4
Pro-49	Isonate M-310	35	-	-	HMDA + DETA	4.5 + 2	17.9
Pro-50	Voranate M-580	84	-	-	HMDA + DETA	12 + 5	-
Pro-51	Voranate M-580	42	-	-	HMDA + DETA	6 + 5.5	-
Pro-52	Voranate M-580	42	-	-	HMDA + DETA	6 + 5.5	-
Pro-53	Voranate M-580	42	-	-	HMDA + DETA	6 + 5.5	17.5
Pro-54	Voranate M-580	42	-	-	HMDA + DETA	6 + 5	-
Pro-55	Voranate M-580	42	-	-	HMDA + DETA	6 + 5.5	-
Pro-56	Voranate M-580	42	-	-	HMDA + DETA	6 + 5.5	-
Pro-57	Voranate M-580	42	-	-	HMDA + DETA	6 + 5.5	-
Pro-58	Voranate M-580	42	-	-	HMDA	5	-
Pro-59	Voranate M-580	42	-	-	HMDA + DETA	6 + 5	-
Pro-60	Voranate M-580	42	-	-	HMDA + DETA	6 + 5	-
Pro-71	Voranate M-580	42	-	-	DEA	12	-
Pro-72	Voranate M-580	14	-	-	HMDA + DETA	2 + 1.7	-
Pro-72(a)	Voranate M-580	42	-	-	HMDA + DETA	6 + 5.5	-
Pro-73	Voranate M-580	42	-	-	HMDA + DETA	2 + 6	14.4
Pro-74	Voranate M-580	42	-	-	TEPA + DETA	9 + 5.2	-
Pro-75	Isonate M-301	35	-	-	TEPA	5	-
Pro-76	Voranate M-580	42	-	-	HMDA + TEPA	1 + 2	10.9
Pro-77	Voranate M-58	42	-	-	HMDA	3	17.8
Pro-78	Voranate M-580	84	-	-	HMDA + DETA	6 + 5	18.2
Pro-79	Voranate M-580	35	-	-	HMDA + DETA	6 + 5	-
Pro-80	Voranate M-580	70	-	-	HMDA + DETA	4.8 + 3	-
Pro-81	Voranate M-580	46	-	-	HMDA	3	-
Pro-82	Voranate M-580	35	-	-	TEPA + EDA	5 + 3	-
Pro-83	Voranate M-580	35	-	-	EDA + DETA	6.2 + 5.6	10.3
Pro-84	Voranate M-580	35	-	-	HMDA + DETA	3 + 3	-
Pro-85	Voranate M-580	35	1,4-BD + TMP	2 + 1	-	-	12.2
Pro-86	Isonate M-342	42	-	-	HMDA	3	-
Pro-87	Voranate M-580	30	Bayflex 2200B	5	1,4-BD + TMP	2.4 + 1	-
Pro-88	Voranate M-580	37	Bayflex 2200B	5	1,4-BD + TMP	2.4 + 1	6.3
Pro-89	Voranate M-580	30	Bayflex 2200B	5	EDA + DETA	6.2 + 5.6	-
Pro-90	Voranate M-580	30	Bayflex 2200B	5	TEPA	4	-
Pro-91	Voranate M-580	42	-	-	DETA	3	10.6
Pro-92	Voranate M-580	42	-	-	TEPA + HMDA	9.6 + 6	17.1
Pro-93	Voranate M-580	42	-	-	DETA + EDA	5.7 + 6.2	19.1
Pro-94	Voranate M-580	35	-	-	DETA + EDA	5.7 + 6.2	-
Pro-95	Voranate M-580	42	-	-	TEPA + EDA	9.6 + 2	17.6
Pro-96	Voranate M-580	42	-	-	EDA + DETA	6.2 + 5.7	16.3
Pro-97	Voranate M-580	42	-	-	HMDA + TEPA	5 + 9.6	15.5
Pro-98	Voranate M-580	12.4	-	-	HMDA + TEPA	2 + 4	14.1
Pro-99	Voranate M-580	42	-	-	HMDA + TEPA	5 + 9.6	18.2

Table 1 COMPOSITIONS OF LAYGON FORMULATIONS (continued)

Example no.	Isocyanate		Copolymer polyester		Amines or Alcohols		HPLC (%)
	Type	Amount g	Type	Amount g	Type	Amount g	
Pro-100	Voranate M-580	42	-	-	HMDA + TEPA	6 + 9.6	17.6
Pro-101	Voranate M-580	35	-	-	HMDA + DETA	5 + 5.7	19.6
Pro-102	Isonate M-301	42	-	-	HMDA + DETA	6 + 5.7	17.6
Pro-103	Isonate M-301	35	-	-	HMDA + DETA	5 + 5.7	18.4
Pro-104	Voranate M-580	42	-	-	TEPA + HMDA	9.6 + 6	14.3
Pro-105	Voranate M-580	42	-	-	TEPA + HMDA	9.6 + 6	-
Pro-106	Voranate M-580	210	-	-	TEPA + HMDA	48 + 30	14.9
Pro-107	Voranate M-580	210	-	-	TEPA + HMDA	48 + 30	18.4
Pro-108	Voranate M-580	42	-	-	TEPA + HMDA	9.6 + 6	-
Pro-109	Voranate M-580	42	-	-	TEPA + DETA	9.6 + 5.7	16.3
Pro-110	Voranate M-580	42	-	-	TEPA + TET	9.6 + 6	14.4
Pro-111	Voranate M-580	42	-	-	TETA + HMDA	3 + 6	17.5
Pro-112	Isonate M-342	42	-	-	TEPA + HMDA	9.6 + 6	-
Pro-113	Isonate M-301	42	-	-	TEPA + HMDA	9.6 + 6	-
Pro-114	Isonate M-310	42	-	-	TEPA + HMDA	9.6 + 6	-
Pro-115	Voranate M-580	20 +	-	-	TEPA + HMDA	9.6 + 6	-
	+ Isonate M-342	22	-	-			

HMDA - Hexamethylenediamine

TEPA - Tetraethylenepentamine

DETA - Diethylenetriamine

EDA - Ethylenediamine

TETA - Triethylenetetramine

1,4-BD - 1,4-Butanediol

TMP - Trimethylolpropane

124 g Propoxur

6.4 g Tetramethrin

37.2 g MGK

12.4 g Piperonyl butoxide

360 ml H<sub>2</sub>O

3.6 g PVA

3 g Tinuvin 770

3 g Irganox 1010

30 g Tween-30

14 g Propyleneglycol

**Testing:**

Propoxur was tested by H.P.L.C., all the other ingredients of the mixture were tested by G. C. The wavelengths at which degradation occurred are tested by irradiation with Xenon lamp 1000W.

After the chemical tests the formulations were checked for their efficacy as pesticides on roaches and flies for knock-down effect and for their effect for long periods of time with exposure to sunlight and without sunlight. The toxicity of the formulation was checked on rats, mice and golden orfe fish.

**Equipment**

HPLC	JASCO	PU 980
HPLC	GBC	LC 1110
GC	Varian	3400 CX
Spectrophotometer U. V.	H. P.	8452A
Monochromator	Oriel	

**Analytical methods**

1 Gr. samples were weighed in 25 mls. flasks which contain 5 mls. DMSO. The solution was mixed and the bottle was put into an ultrasonic bath for 15 minutes. After that methanol was added almost to the line and returned to the sonicator for extra 15 minutes. The volume was filled up to 25 mls. with methanol. 1 ml. of the solution was diluted for 25 mls. in methanol and injected to HPLC.

Column RP-18

$\lambda = 220$  n.m.

loop 20 $\mu$ l.

flow 0.8 mls./mins.

sample rate 0.5

Retention time 4 mins.

Eluent: methanol 72%, acetonitril 12% and water 16%.

**Method for GC Determination of Tetramethrin, Piperonyl, Butoxide and MGK**

In 100 mls. measuring flask 0.07 gr. MGK 0.05 gr. piperonyl butoxide, 0.05 gr. tetramethrin 0.05 gr. essential oil of lemon and 0.05 gr. of propoxur were weighed and dissolved in methanol. 1 ml. of the solution mass was diluted in 10 mls. measuring flask. 2  $\mu$ l. of the sample were injected to G. C. apparatus:

column BD-1 1.5 mls.

Carrying gas helium

oven programming initial temperature 180 °C for 5 minutes

final temperature 250 °C

Rate 15 °C per minute

Injector 280 °C

FID detector 300 °C

#### **Retention Time**

MGK 9.4 per minute

Piperonyl butoxide 120. per minute

Tetramethrin - 12.3 per minute

#### **Degradation Tests**

A solution of 100 mgs. Laygon in 100 mls. methanol in quartz tube was irradiated in several wave lengths for 500 hours. The degradation of the Laygon was checked.

#### **Biological tests**

Determination of the formulation efficacy in 50 mls. aquaria.

Walls of the aquaria were sprayed with 0.5% of the diluted formulations and dried. Then 100 flies were put in the aquaria. the mortality of the flies were checked after one, 3, and 24 hours.

This method measures the levels of susceptibility of a population of cockroaches to a given insecticide. Cockroaches are exposed to standard insecticide residues in a petri dish, and mortality is determined. From the results, the times necessary for 50% and 95% knock-down (LT<sub>50</sub> and LT<sub>95</sub>) can be determined. It is preferable to use adult males. If it is not possible to obtain enough males, information on susceptibility can be obtained by using females. The test is carried out in a room free of Insecticidal contamination. The cockroaches are exposed to the insecticide and held at a temperature between 25 °C and 30 °C and at a relative humidity above 25%. Cockroaches *Germanica blatella* were grown in our laboratory in containers with ready-to-serve meaty dog food.

A solution of each of the different formulations and the commercial material is obtained by placing the substances in a high-shear mixer for 5 minutes. Solutions of different concentrations of the pesticide formulations were prepared. For each

formulation Whatman paper No. 41 (d=9 cm.) is dipped into the solution during mixing and put in a petri dish (d=9 cm.). the filter paper for exposure time 0 is dried in a hood and the others are taken to the roof of the laboratory and exposed to sunlight. Approximately every five days a petri dish is removed from the roof, and five *Germanica blattella* cockroaches are placed inside. To introduce five cockroaches into each petri dish, the cockroaches are first anaesthetized with carbon dioxide. The test is performed in three replications and mortality is checked. The exposure times examined were approximately 0, 5, 10, 15 and 20 days. Control dishes - untreated Whatman paper with 5 cockroaches are 24 hours.

A cockroach is considered knocked down if it fails to move on being returned to a normal posture.

The experiments carried out with flies were the same as with cockroaches.

#### **METHOD USED TO DETERMINE ACUTE ORAL MICE TOXICITY**

It is preferable to use adult males (2-2.5 months) weighting 25-30 gr. A solution of the formulation is obtained by placing it in a vortex mixer for 5 minutes.

The quantity of the solution depends on the weight of the mouse, 1 ml. of solution being used for 20 gr. weight of mouse. The solution is introduced by using syringes (2 mls.) via the mouth into the stomach of each mouse. The test is performed in five replications and mortality is checked after 0, 5, 24, 48, 72, 96, 120, 144 and 168 hours. Standardized mouse food is given during the experiment.

The tests were carried out according to World Health Organization Technical Report Series No. 443 Geneva 1970 p. 130-133.

#### **METHOD USED TO DETERMINE FISH TOXICITY (GOLDEN ORFE) TO PESTICIDES**

A gold orfe fish requires about the same basic care: water quality as close as possible to pH = 7.0 (neutral); water temperature about 24 °C to 25 °C), 10 fish/aquarium. The fish were given adequate and standardized food (Europet Basic food) before and after the experiment. Food was withheld for two days before the experiment.

Solutions of formulation and commercial material are obtained by placing the substance in a high-shear mixer for 5 minutes. Solutions of 250; 500; 1000; 2000; 4000; 5000; 10,000; 20,000 and 40,000 µg/liter of pesticide formulation are



prepared. Mortality is checked after 3, 6, 24, 48, 72 and 96 hours. From the results, the times necessary for 50% and 95% mortality ( $LT_{50}$  and  $LT_{95}$ ) can be determined for each formulation.

#### Determination of toxicity to Rats

Male rats with weight 150-160 grs. were taken to the experiment. Solutions of the various formulations were introduced by using a syringe through the mouth into the stomach of the rat. For each experiment 208 rats were tested and the experiment was done with three replicas.

The mortality of the rate was checked out after 1, 3, 24, 48, 72, 96, 168 hours before the experiment only water was given to the rats and during the experiment the rats were given standardized food.

The results of the above tests are set forth in Tables 2-19 hereinafter.

Table 2 Percentage Mortality of (*Blattella germanica*) resulting from various Laygon Formulations

Various Laygon Formulations									
Form. No.	Laygon (%)	A.I.	Content. p.p.m						Cont.
			100	300	500	800	1000	1500	
Pro-1	17.4		8	24	88	92	100	-	0
Pro-3	17.6		0	36	88	100	100	-	
Pro-4	19.8		-	-	53	93	-	-	
Pro-5	19.7		-	-	67	100	-	-	
Pro-6	18.3		-	-	40	93	-	-	
Pro-7	21.6		-	-	33	93	-	-	
Pro-8	20.4		-	-	33	93	-	-	
Pro-5 (II)	20.1		-	-	100	100	-	-	
Pro-5 (II)	19.2		-	-	100	100	-	-	
Pro-27	20.4		-	-	80	93	100	-	
Pro-31	20.3		-	-	-	45.3	59.3	84	
Pro-77	17.8		-	-	-	66.7	100	-	
Pro-78	18.2		-	-	-	100	100	-	
Pro-92	17.1		-	-	-	100	100	-	
Pro-99	18.2		-	-	-	84	93.3	-	
Pro-100	17.6		-	-	-	92	100	-	
Technical Pro-10	98		4	28	32	80	100	100	
Mixture •Pro-77	100		-	-	-	6.7	20	-	
Mixture •Pro-78	100		-	-	-	26.7	33.3	-	
Mixture •Pro-99	100		-	-	-	8	40	-	
Mixture •Pro-100	100		-	-	-	12	44	-	

Mixture without organic solvent•

**Table 3 Percentage Mortality of (*Blattella germanica*) resulting from various Laygon Formulations 24 Hour Exposure**

Form. No.	A.I. (%)	Concent. ppm		Cont.
		800	1000	
Pro-107	29.65	70	95	0
Mixture (with org. solvent) Pro-107	100	92	96	
Pro-103	31.12	60	93.3	
Mixture (with org. solvent) Pro-107	100	60	93.3	

**Table 4 Percentage Mortality of (*Blattella germanica*) resulting from various Laygon Formulations 1,00 ppm. which were Exposed to Sunlight**

Exposure to sunlight days	Form. No.		Cont.
	Pro-107	Mixture Pro-107-5 (with org. solvent)	
0	100	100	0
5	100	100	
11	100	92	
18	88	84	
25	0	0	

**Table 5 Percentage Mortality of (*Blattella germanica*) resulting from various Laygon Formulations 24 Hour Exposure**

Form. No.	A.I. Laygon (%)	Concent. ppm				Cont.
		50	100	200	300	
Pro-27	20.4	10	40	96.7	100	0
Pro-31	20.3	-	53.3	60	93.3	
Tech. Propoxur	98	-	10	83.3	90	

**Table 6 Percentage Mortality of (*Blattella germanica*) resulting from various Laygon Formulations in aquaria. Fifty Adult Roaches were placed in each aquarium.**

Exposure time (h)	Encapsulated Pro-117	Non. encapsulated (in org. solvent)-	Control
	Solution Concentration (ppm)		
0	0	0	0
3	100	90	
6	-	100	

**Table 7 Percentage Mortality of the house fly (*Musca domestica*) resulting from various Laygon Formulations**

Exposure time (h)	Encapsulated Pro-117	Non. encapsulated	Control
		(in org. solvent)	
		Solution Concentration (ppm)	
0	0	0	0
2	17.3	23	
24	100	100	

**Table 8 Percentage Mortality of (*Blattella germanica*) resulting from various Laygon Formulations (24 hours Total exposure time)**

Formulation No.	concentration of active org. (%)	Solution concentration		Control
		800	1000	
Encapsulated Pro-107	25.2	100	100	0
Non. encapsulated Pro-107	100		100	

Table 9 Percentage Mortality of Mice due to various Laygon Formulations  
(a.i. of Laygon/mg)

Exposure to material  (h)	Formulation No.																						
	Tech Laygon					Pro-1		Pro-3		Pro-4		Pro-6		Pro-7		Pro-8		Pro-5			Pro-5 (II)		
	10	15	20	25	50	60	60	60	60	60	60	60	60	100	160	200	60	100	120	140			
0.5	1/2	3/9	5/12	4/5	2/2	0/2	2/2	2/2	2/2	1/2	2/2	2/2	0/2	0/2	5/7	2/2	2/2	2/2	2/2	2/2			
10	1/2	3/9	5/12	4/5	-	0/2	-	-	-	1/2	-	-	0/2	0/2	5/7	-	-	-	-	-			
24	1/2	3/9	5/12	4/5	-	0/2	-	-	-	1/2	-	-	0/2	0/2	5/7	-	-	-	-	-			
48	1/2	3/9	5/12	4/5	-	0/2	-	-	-	1/2	-	-	0/2	0/2	5/7	-	-	-	-	-			
168	1/2	3/9	5/12	4/5	-	0/2	-	-	-	1/2	-	-	0/2	0/2	5/7	-	-	-	-	-			

Table 10 Percentage Mortality of Mice due to various Laygon  
Formulations (a.i. of Laygon/mg)

Exposure to material (h)	Formulation No.																							
	Pro-5 (III)			Pro-13			Pro-14		Pro-15I		Pro-17		Pro-19I		Pro-20		Pro-22		Pro-23		Pro-24		Pro-25	
	60	100	60	100	100	60	100	60	60	60	100	60	60	60	60	60	60	60	60	60	60	100		
0.5	2/2	2/2	0/7	2/2	2/2	2/2	2/2	2/2	0/2	5/7	2/2	2/2	2/2	2/2	1/2	2/2	1/2	2/2	2/2	1/2	2/2			
10	-	-	5/7	-	-	-	-	-	0/2	5/7	-	-	-	1/2	-	1/2	2/5							
24	-	-	5/7	-	-	-	-	-	0/2	5/7	-	-	-	1/2	-	1/2	2/5							
48	-	-	5/7	-	-	-	-	-	0/2	5/7	-	-	-	1/2	-	1/2	2/5							
168	-	-	5/7	-	-	-	-	-	0/2	5/7	-	-	-	1/2	-	1/2	2/5							

Table 11 Percentage Mortality of Mice due to various Laygon Formulations (a.i. of Laygon/mg)

Exposure to material (h)	Formulation No.																			
	Pro-26				Pro-27-29				Pro-31				Pro-33				Pro-40-43			
	60	70	75	80	60	70	60	60	70	60	70	60	60	60	60	60	60	60	60	60
0.5	0/2	0/2	1/2	2/2	2/2	5/5	2/2	1/2	1/5	1/2	2/2	2/2	2/2	2/2	1/2	2/2	1/2	2/2	2/2	2/2
1.0	0/2	0/2	1/2	-	-	-	-	1/2	1/5	2/2	-	-	-	-	1/2	-	1/2	-	-	-
24	0/2	0/2	1/2	-	-	-	-	1/2	1/5	-	-	-	-	-	1/2	-	1/2	-	-	-
48	0/2	0/2	1/2	-	-	-	-	1/2	1/5	-	-	-	-	-	1/2	-	1/2	-	-	-
168	0/2	0/2	1/2	-	-	-	-	1/2	1/5	-	-	-	-	-	1/2	-	1/2	-	-	-

Table 12 Percentage Mortality of Mice due to various Laygon Formulations (a.i. of Laygon/mg)

Exposure to material (h)	Formulation No.											
	Pro-26		Pro-78		Pro-83		Pro-85		Pro-92		Pro-96	
	40	60	40	60	40	40	40	50	40	50	40	40
0.5	3/5	2/2	3/7	2/2	2/2	4/5	0/2	2/5	2/2	5/5	2/2	2/2
1.0	3/5	-	3/7	-	-	4/5	0/2	2/5	-	-	-	-
24	3/5	-	3/7	-	-	4/5	0/2	2/5	-	-	-	-
48	3/5	-	3/7	-	-	4/5	0/2	2/5	-	-	-	-
168	3/5	-	3/7	-	-	4/5	0/2	2/5	-	-	-	-

Table 13 Percentage Mortality of Mice due to various Laygon Formulations (a.i. of Laygon/mg)

Formulation No.															
Exposure to material (h)	Pro-77		מגון Pro-77-5		Pro-78		Mixture Pro-77-5		Pro-92		Mixture Pro-77-5		Tecn. Laygon		
	mg/mixture/kg/body weight												mg/ Laygon/ Kg. body weight		
	60.5	90	10	20	61.5	92.5	10	20	61	70	10	20	15	20	25
0.5	3/5	2/2	2/5	4/10	3/7	2/2	2/5	2/5	0/2	8/15	4/9	2/2	0/5	1/5	4/5
10	3/5	-	2/5	5/10	3/7	-	2/5	2/5	0/2	8/15	4/9	-	0/5	1/5	4/5
24	3/5	-	2/5	5/10	3/7	-	2/5 <sup>1</sup>	2/5	0/2	8/15	4/9	-	0/5	1/5	4/5
48	3/5	-	2/5	5/10	3/7	-	2/5	2/5	0/2	8/15	4/9	-	0/5	1/5	4/5
168	3/5	-	2/5	5/10	3/7	-	2/5	2/5	0/2	8/15	4/9	-	0/5	1/5	4/5

Table 14 Percentage Mortality of Mice due to various Laygon Formulations (a.i. of Laygon/mg)

Exposure to material (h)	Formulation No.																	
	Pro-99								Pro-100	mixture	Pro					mixture		
									Pro-100-5	Pro-100-5	101	102	103	104	106	Pro-103-5		
	mg/mixture/kg/body weight																	
	50.8	62.5	70	75	20	25	30	54	20	70	70	70	70	70	10	15	20	
0.5	1/2	0/2	6/15	2/2	0/2	2/5	2/5	2/2	2/2	2/2	2/2	4/7	2/2	5/5	0/2	1/5	2/2	
10	1/2	0/2	7/15	-	0/2	2/5	2/5	-	-	-	-	4/7	-	-	0/2	1/5	-	
24	1/2	0/2	8/15	-	0/2	2/5	2/5	-	-	-	-	4/7	-	-	1/2	2/5	-	
48	1/2	0/2	8/15	-	0/2	2/5	2/5	-	-	-	-	4/7	-	-	1/2	2/5	-	
168	1/2	0/2	8/15	-	0/2	2/5	2/5	-	-	-	-	4/7	-	-	1/2	2/5	-	

Table 15 Percentage Mortality of Mice due to various Laygon Formulations (a.i. of Laygon/mg)

Exposure to material  (h)	Formulation No.										
	Pro-107	mixture			Pro-109	Pro-110	Pro-111	Pro-107			
	mg/mixture/kg body weight										
	80	25	30	70	70	70	30	50	70	80	90
0.5	1/2	0/2	6/15	2/2	0/2	2/5	2/2	2/2	2/2	2/2	4/7
10	1/2	0/2	7/15	-	0/2	2/5	-	-	-	-	4/7
24	1/2	0/2	8/15	-	0/2	2/5	-	-	-	-	4/7
48	1/2	0/2	8/15	-	0/2	2/5	-	-	-	-	4/7
168	1/2	0/2	8/15	-	0/2	2/5	-	-	-	-	4/7

Table 16 Percentage of rate/total Number of Rats after exposure to Laygon formulation (a. i. of Laygon/mg)

Exposure to material (h)	Formulation No.											
	Pro-107-5 Mixture								Pro-107			
	mg/mixture/kg body weight											
	160	120	118	115	110	100	80	50	285	260	240	230
0.5	2/2	3/5	1/5	0/2	0/5	0/2	0/2	0/2	2/2	2/2	4/5	1/7
1.0	-	3/5	1/5	0/2	0/5	0/2	0/2	0/2	-	-	4/5	1/7
24	-	3/5	1/5	0/2	0/5	0/2	0/2	0/2	-	-	4/5	1/7
48	-	3/5	1/5	0/2	0/5	0/2	0/2	0/2	-	-	4/5	1/7
168	-	3/5	1/5	0/2	0/5	0/2	0/2	0/2	-	-	4/5	1/7



Table 17 Percentage Mortality of Mice after exposure to Laygon Formulations

Exposure to material (h)	Formulation No.			
	Non. encapsulated Pro-117		Encapsulated mixture Pro-117	
	(mg) mixture/kg body weight			
	25	30	50	70
	0.5	2/5	3/5	1/5
0.1	2/5	3/5	1/5	3/5
24	2/5	3/5	1/5	3/5
48	2/5	3/5	1/5	3/5
168	2/5	3/5	1/5	3/5

Table 18. Percentage Mortality of Mice after exposure to Laygon formulations

Exposure to sun day	Exposure to material (h)	Formulation No.			
		Pro-117-5 Mixture		Pro-117	
		(mg) mixture/kg body weight			
		25	70	50	30
0	0.5	0/5	3/5	-	-
	0.5	1/5	3/5	-	-
	0.5	1/5	3/5	-	-
	0.5	1/5	3/5	-	-
11	0.5	0/5	5/5	3/5	0/5
	24	1/5	-	3/5	0/5
	48	1/5	-	3/5	0/5
	168	1/5	-	3/5	0/5

**Table 19 Percentage Mortality of Mice after exposure to Laygon Formulations**

Formulation No.										
Exposure to material (h)	Pro-107					Pro-107-5 Mixture				
	(mg) mixture/kg body weight									
	30	50	70	80	90	10	15	25	30	40
0.5	0/5	1/5	2/5	4/5	5/5	1/5	1/5	2/5	3/5	5/5
10	0/5	1/5	2/5	4/5	-	1/5	1/5	2/5	3/5	-
24	0/5	1/5	2/5	4/5	-					
48	0/5	1/5	2/5	4/5	-					
168	0/5	1/5	2/5	4/5	-					

Referring now to the single figure attached hereto there is shown LD 50 for mice with an encapsulated formulation of the present invention in comparison with a non-encapsulated Laygon mixture.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments and examples be considered in all respects as illustrative and not restrictive, reference being made to the appended claims, rather than to the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

**WHAT IS CLAIMED IS:**

1. A process for encapsulating a mixture of propoxur, tetramethrin, piperonyl butoxide, N-octyl-bicycloheptene-dicarboximide (MGK) and essential oil of lemon (laygon) in a micro-capsular formulation comprising:

a) providing a first solution of water and polyvinyl alcohol (PVA) and heating to about 50-60° C;

b) providing a second organic solution comprising a mixture of melted laygon and an isocyanate;

c) emulsifying said second mixture in said first mixture;

d) adding an aqueous solution of a polyfunctional amine with agitation to said emulsion said solution containing about 10% - 40% of the stoichiometric amount by weight of amine necessary to fully react with said isocyanate;

e) adding an oxyethylated monooleate sorbate emulsifier to prevent coagulation of the reaction mixture;

f) adding the remaining polyfunctional amine solution over a period of between 5 to 10 minutes;

g) reducing the temperature of the reaction mixture to about 20° - 40° C; and,

h) adding a weak polyfunctional acid to neutralize the solution to a pH of about 7.0-8.0

2. A process according to claim 1 wherein in step d said aqueous solution contains about 20% - 30% of the stoichiometric amount by weight of amine necessary to fully react with said isocyanate;

3. A process according to claim 1 where at least one UV absorbent material is included in the organic solution of step b.

4. A process according to claim 1 further comprising an additional step of adding a mixture of propylene glycol, soap and gums.

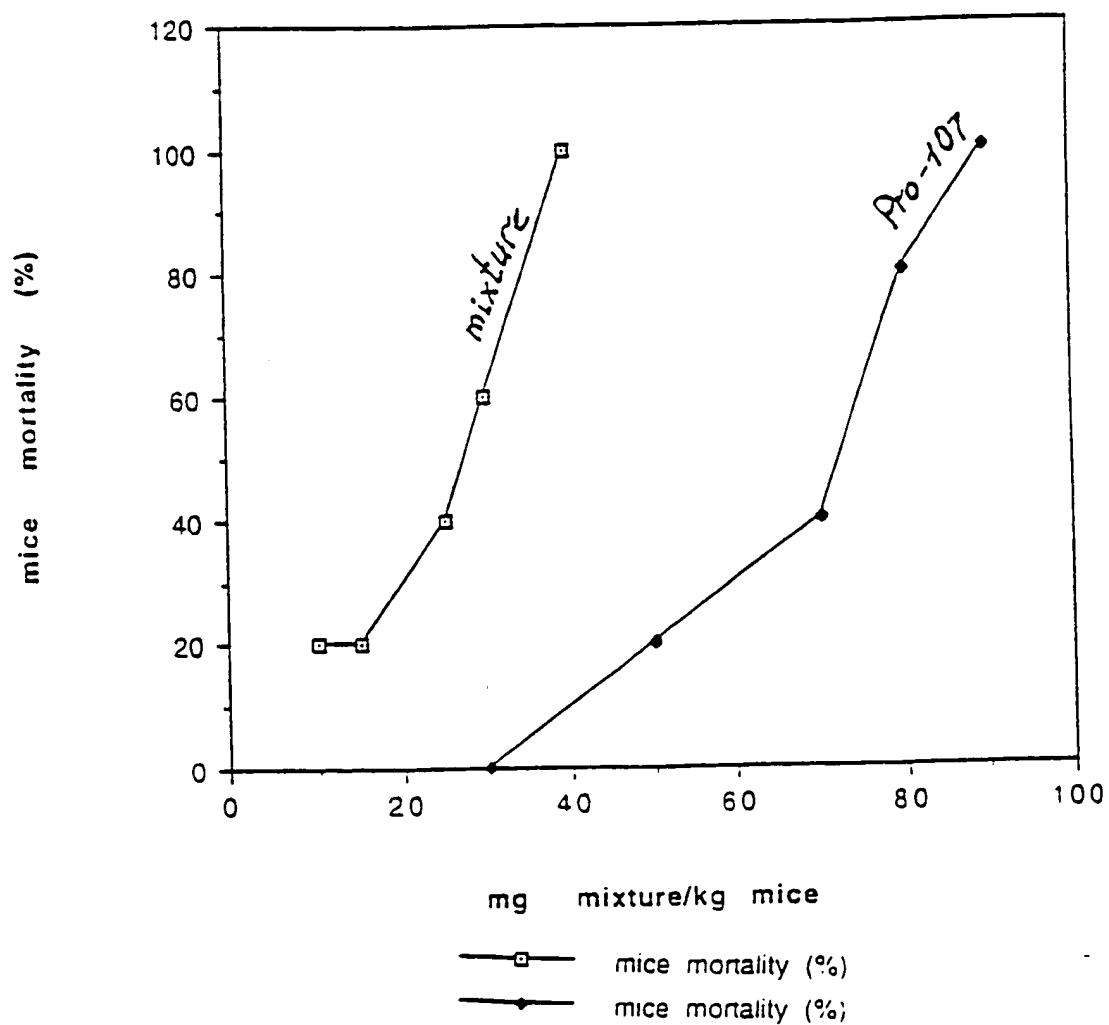
5. A process according to claim 4 wherein said gums are selected from the group consisting of xanthan, guar, caraya and mixtures thereof.

6. A process according to claim 1 wherein said polyfunctional acid is selected from the group consisting of citric acid, ascorbic acid and phosphoric acid.

7. A process according to claim 1 wherein said isocyanate is 4,4-diphenyl methane diisocyanate.
8. A pesticidale composition comprising encapsulated Laygon as active ingredient therein whenever prepared according to the process of claim 1.

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## LD 50 For mice with Encapsulated Formulation Pro-107



# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/IL 98/00177

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N53/10 A01N25/28 B01J13/16 //(A01N53/10,47:22,43:30,37:32)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 183 999 A (PENNWALT CORP) 11 June 1986 see page 4, line 3 - page 6, line 13; claim 1; example 1 ---	1-8
A	GB 2 187 957 A (SUMITOMO CHEMICAL CO) 23 September 1987 see page 1, line 5 - line 12 see page 2, line 12 - line 20; examples 1,10 ---	1-8
A	US 4 851 227 A (MARKUS ARIE ET AL) 25 July 1989 see column 1 - column 3, line 36 --- -/--	1-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

3 September 1998

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/IL 98/00177

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 23506 A (UNIV BEN GURION ;COHEN A DAVID (IL); MARCUS ARIE (IL)) 8 September 1995 see page 1 - page 3, line 4; example 1 ---	1-8
A	EP 0 165 227 A (MONSANTO CO) 18 December 1985 see page 1 - page 9, line 22; examples ---	1-8
A	A.C. APPEL : "Knockdown Efficiency and Materials' Compatibility of Wasp and Hornet Spray Formulations to Honey Bees (Hymenoptera: Apidae)" JOURNAL OF ECONOMIC ENTOMOLOGY, vol. 83, no. 5, October 1990, pages 1925-31, XP002076405 COLLEGE PARK, MD, US see page 1926, table 1, Brand: "Marko" -----	1-6

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